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CORROSION FATIGUE OF A HEAT TREATED DUPLEX STAINLESS STEEL IN PAPER MACHINE WHITE WATERS

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ABSTRACT

The present study addresses the corrosion fatigue behavior of a duplex stainless steel (DSS) material used for suction rolls at the wet end of paper machines during pulp and paper manufacturing. Environments that reflect increments of chloride ion concentration, as effect of water closure (volume of water used per ton of paper produced), were studied as well as different microstructures that might be obtained during manufacturing or repair of the DSS roll materials. Standard corrosion fatigue tests were conducted using compact tension specimens by measuring the crack growth with the number of fatigue cycles and calculating the stress intensity change (driving force) for crack growth under realistic environments. Results from this study clearly indicate that for the tested duplex stainless steel, microstructural changes due to heat treatment had more effect on the threshold stress intensity for crack propagation and on crack growth rates than did the increase in chloride ion concentration in paper mill environments. Increase in chloride ion concentration had a small effect on lowering of threshold stress intensity change, ΔK_{th}, or all heat treatments; however, one of the reasons for the insignificant effect of the environment on corrosion fatigue behavior of DSS's might be the test parameters. The experiments presented in this study were conducted at 25 Hz in a tension/tension sinusoidal waveform to a R=0.5 ($R = \sigma_{min}/\sigma_{max}$). Under high frequency, the crack tip may not be exposed to the aggressive environment long enough to be affected by crack propagation and growth rates. Lower cycling frequencies will expose the crack opening for longer periods to the aggressive environment and may exhibit a detrimental effect on the corrosion-fatigue crack behavior. Environments, which cause localized corrosion in DSS (e.g., higher chloride ion concentration in white waters), may show a significant effect on the fatigue life of DSS rolls as pits may act as initiation sites for cracks as well as precipitates in crack growth. This effect may also be more pronounced at lower frequencies as the crack tip will be exposed to the corrosive environment for longer time periods in each cycle.

Keywords:
Duplex Stainless Steel, Heat Treatment, Corrosion, Fatigue, Paper Machines, Suction Roll, Second Phase Particles, Carbides, Ferrite, Austenite.

1. INTRODUCTION

The Institute of Paper Science and Technology is an independent, privately supported institution devoted to education and research in engineering and the natural sciences, particularly as applied to the pulp and paper industry. The academic programs, leading to the degrees of master of science and doctor of philosophy degrees, are particularly noted for their breadth and multidisciplinary

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nature. The purpose is to develop a "scientific generalist" who is well versed in several disciplines relevant to paper science and technology. Research at IPST covers all areas of papermaking and related processes, from the growth of trees and other fiber sources, through the manufacture of pulp and paper, to the recycling of paper and the recovery of papermaking chemicals and the study of corrosion and materials used in the manufacturing processes.

Pulp and paper mills are susceptible to many forms of corrosion, necessitating specialized material selection. In paper machines, suction rolls are used to remove water from paper at the wet end of the paper machine. One way to accomplish this is by passing the paper web through a roll nip, one roll of which is called the suction roll (Figure 1 [1]). The suction roll is typically drilled to an area of 20% and a vacuum is applied to the inside to remove water [1]. The critical component in the suction roll configuration is the drilled shell, which is subjected to corrosion fatigue.

Corrosion fatigue is the combination of cyclic stresses and a corrosive environment. No metal is immune to some reduction of its resistance to cyclic stresses if it is corroded by the environment in which it is stressed. The damage from corrosion fatigue is synergistic and, in turn, greater than the damage arising from either fatigue or corrosion independently [2].

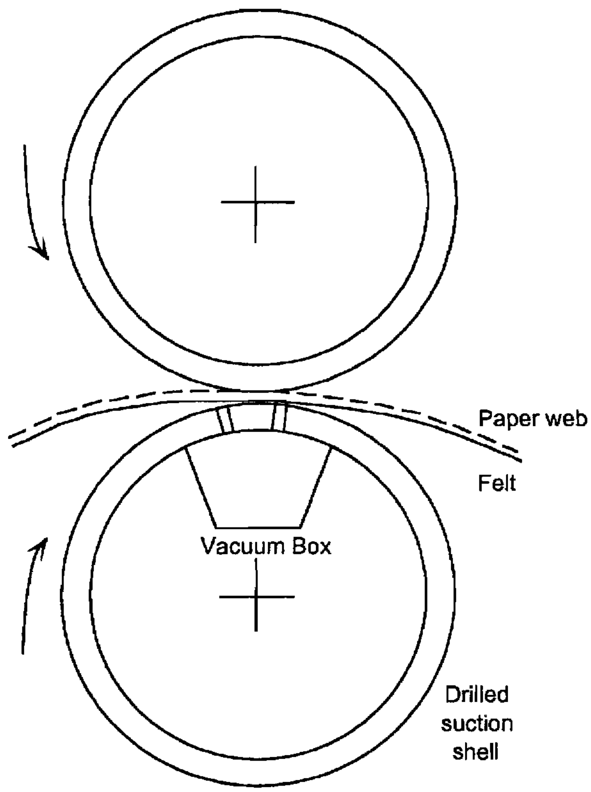


Fig. 1. Cross section of suction roll configuration [1].

History of Suction Roll Materials

In the early days of modern paper machines, prior to 1950, suction rolls were cast from bronze. Bronze was in general a good material due to its castability, machinability, corrosion resistance, and relatively low cost. However, bronze lacked the strength needed to resist the higher press loads and the stiffness necessary to maintain shape and roundness when larger paper machines were introduced. Suction roll nip pressures increased from 26 KN/m up to 79 KN/m by 1964 [1]. Pressures of up to 131 KN/m were achieved in the 1970's. Also, widths increased from 3.8 m (1950's) to an excess of 10 m in the 1970's.

The first stainless steel materials to be widely used were forged type 400 martensitic alloy and centrifugally cast CF-3M and CF-8M austenitic alloys. From 1955 to 1965, the influence of corrosion fatigue was not widely recognized, since rolls were designed according to the strengths of these alloys in air [3].

In 1957, the first centrifugally cast CA-15 martensitic stainless steel shells were cast. Also, alloy A-63 and aluminum bronze rolls were introduced.

Between 1969 and 1977, DSS69, C169, alloy 70 (martensitic) and A170, A171, A271 and A-75 (duplex, ferritic–austenitic) were introduced. Also alloys such as rolled and welded SS 316 and 3RE60 appeared. Continuous cast bronzes GC type also emerged.

In 1971, fatigue strength reduction was reported for bronze and stainless steel tested in synthetic water [4]. During the end of the seventies and eighties, new stainless steels were introduced. These included centrifugally cast precipitation hardening duplex alloys VK-A378 and KCR-A682 and duplex alloys A-86 and ACX-100.

Cracking of suction rolls has been chronic for the paper industry in recent decades. However, the extent of the problem has not been well documented. Only a few studies report failures in suction rolls of all types [5-7], the most frequent being bronze and martensitic stainless steels. In particular, duplex stainless steels have not been reported as susceptible to corrosion fatigue in the early work published in the eighties and in some exploratory work conducted in simulated "TAPPI" water [8]. But with the increasing degree of mill closure, bleaching carry-over problems, and the accumulative damage caused by cyclic loading in specific metallurgical microstructures over the years, suction rolls might fail.

The characteristics of failure vary from roll to roll, but circumferential cracking in the middle of the roll predominates. Cracking may begin at the inside or outside surface of the roll shell, but cracking at the inside surface is apparently more common [7]. Figure 2 shows how cracks grow from inside the suction roll holes. Nearly all cracking is confined to the middle two thirds of the shell, where the largest bending moments are thought to occur. In terms of the environment, there have been few studies that correlate suction roll fatigue failure with metallurgy/fabrication and white-water characteristics [7-9].

White-Water Environments

Suction rolls are subjected to a variety of corrosive environments. The severity of the environment depends primarily on the type of paper produced and the degree of closure (volume of water used per ton of paper produced). Bacterial corrosion can occur specially in creviced areas, such as suction roll holes filled with pulp, where biocides cannot reach. The corrosivity of white water depends primarily on the pH, temperature and the concentrations of aggressive inorganic anions, such as chloride and thiosulfate. Chloride concentration increases with closure and causes pitting of the metal. [1]. Sulfate ions, however, are not considered aggressive, and they are thought to shield the effect of pitting when found in larger molar concentrations than chloride. Nonetheless, sulfate increases conductivity of the solution and hence environment corrosivity [10-12]. Additionally, if sulfate-reducing bacteria are present, sulfate will indirectly promote localized corrosion [13]. Another critical anion in the pitting process is thiosulfate ion. Thiosulfate ions arise from hydrosulfite solutions used for brightening. The warm decomposition from those solutions will increase the amount of thiosulfate due to the slow kinetics of oxidation to form more stable sulfate.

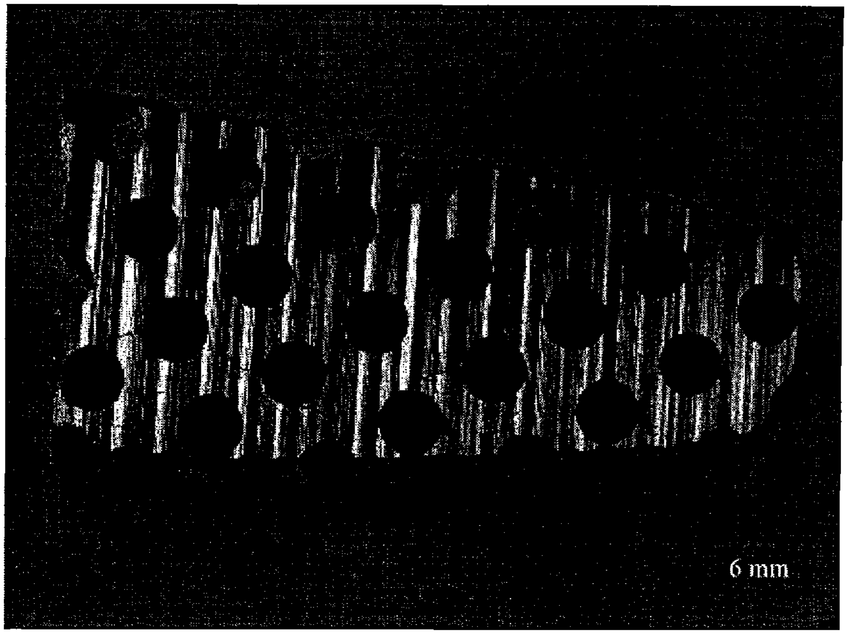


Fig. 2. Suction roll sample of failed DSS (inside surface view).

The worst case of thiosulfate pitting occurs within the molar concentration ratio range [13]:

$$\frac{Na_2SO_4 + NaCl}{Na_2S_2O_3} = 10 - 20 \tag{1}$$

Above the range presented by the ratio in Eq. (1), there is insufficient thiosulfate to reach the pit nucleus. Below this range, there is too much thiosulfate reduction to bisulfate, which would prevent the acidification of the pit required for further growth.

Crack Initiation and Propagation in Corrosion Fatigue

Suction roll lifetime may be split into two stages: crack initiation and propagation. Fatigue crack initiation may occur by irreversible localized deformation produced by cyclic loading forming intrusions and extrusions [14]. In the case of an aggressive environment (e.g., white waters), pitting will speed up the process since it will generate heterogeneities at the surface of the metal such as pits and the environment within the pit (localized) may be more aggressive than the bulk solution. Many studies have addressed the onset of pitting for the case of paper machine materials, which would give some confidence in terms of crack nucleation processes [11-18]. Others have looked at the cyclic effects on crack initiation in relatively benign environments through S-N curves [19-20]. Few studies [7-9], however, have addressed both crack initial growth and propagation under severe environmental conditions, which is clearly an important step in assessing suction roll failure.

It is known that the rate of crack growth during fatigue loading depends on the magnitude of the cyclic forces, frequency, instantaneous crack length, geometry of the crack and material. The environment would play a role below the threshold cyclic intensity range, ΔK_{th}. Below threshold, the crack growth rates are so slow they are almost impossible to measure (under 10^{-8} m/cycle, which approximates atomic distance [21]). The value of "ΔK" represents the change of stress intensity of a material in a cycle and relates the far-field stress change, $\Delta\sigma$, of a material with crack size, a, according to the following relationship developed for Linear Elastic Fracture Mechanics (LEFM) [14, 21]:

$$\Delta K \propto \Delta\sigma\sqrt{\Pi a} \tag{2}$$

The proportionality of the above equation is corrected once the geometry of the specimen and crack taken into account. The stress intensity change denotes the driving force for crack growth and it is useful to predict the rate of crack growth in service. Three stages are often evidenced in a log - log crack growth rate plot versus stress intensity change (Figure 3).

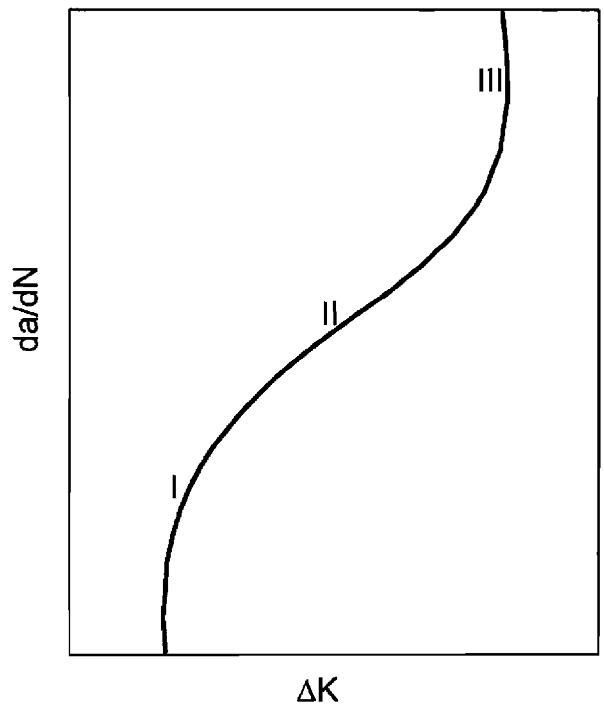


Fig. 3. Crack growth rate data vs. stress intensity change [21].

Region I of the sigmoidal crack growth rate is associated with threshold effects. Below the value of threshold stress intensity factor, fatigue crack growth does not take place, and if it does it happens at a rate too small to measure (spacing between atoms). The threshold stress intensity change depends on the "R" ratio ($R = \sigma_{min}/\sigma_{max}$), the frequency of the applied stress and the environment. Aggressive environments in particular might shift the whole curve (including threshold stress) to the left and upward.
Region II follows almost a straight line and fits the following equation, proposed by Paris [14, 21]:

$$\frac{da}{dN} = C(\Delta K)^m \tag{3}$$

"C" and "m" are usually materials constants found in the literature according to ASTM standards [22, 23].

Usually the fatigue life is not sensitive to the fracture toughness of the material. However, aggressive environments might increase the crack growth rates by an order of magnitude.

Region III represents unstable crack growth caused by over loading the material and has no significant effect on crack propagation life. This region is dependent on yield stress, stress intensity and stress ratio. The following equation applies [21]:

$$\frac{da}{dN} = \frac{C(\Delta K)^m}{(1-R)K_c - \Delta K} \tag{4}$$

Where K_c is related to the material toughness.

DSS Metallurgy

DSS alloys contain equal volume fractions of ferrite (chromium rich) and austenite (nickel rich). The trend is to reduce carbon and nickel levels by increasing that of nitrogen. This has led to significant improvements in corrosion resistance and structural stability [24]. Also, the presence of ferrite (absent in austenitic steels), minimizes hot cracking produced during casting [25].

Where DSS have replaced austenite stainless steels, it is because of superior corrosion resistance and stress corrosion resistance. They are useful in highly oxidizing environments, chloride environments and those containing H_2S. Duplex stainless steels have therefore earned a place in chemical plants, in the pulp and paper industry, in the oil and gas industry, in marine environments, and in heat exchangers [25].

The mechanical properties of DSS surpass other stainless steels in terms of tensile properties (up to three times that of regular austenitic and ferritic at room temperature) and low expansion coefficients [26]. Numerous microstructural changes can occur in DSS during isothermal or anisothermal heat treatments. Most of these transformations are concerned with the ferrite, as element diffusion rates are approximately 100 times faster than in austenite. The presence of elements such as Cr and Mo in ferrite promote the formation of both intermetallic phases as well as precipitation caused by the low solubility of elements in it during heat treatments [26]. The presence of those phases may not only affect the mechanical properties of the DSS's but also the corrosion resistance.

It is then of utmost importance to determine both the possible phase diagrams and Time Temperature Transformation (TTT) diagrams of such steels. Because of the complexity of ternary phase diagrams it is necessary to approach the problem by simplifying it. One approach has been to produce isothermal sections of the Fe-Cr-Ni-Mo-N using a computer program named *Thermocalc*™ to produce a pseudo binary diagram with Ni and Cr contents [27]. This has certainly helped a great deal with interpreting phase formation during equilibrium. However, the problem has not been solved completely since most DSS are heat treated for service. Few authors have attempted to provide TTT diagrams for DSS [28, 29]. In general, several phases may form depending on the temperature and composition to which different DSS's have been subjected. Some of the phases of interest have been identified for DSS U50 and might be present in other DSS's [24-29].

The corrosion properties of DSS's depend on the ability to passivate and remain passive during service. Alloy design may in fact alter the corrosion behavior of duplexes, especially when general corrosion is taking place. The onset of pitting is of most importance during corrosion fatigue since this alone will decrease the endurance limit for fatigue resistance [24]. According to Parkins [30], the minimum stresses for initiation are lowered by the effect of pitting corrosion. In corrosion-fatigue, crack initiation is favored by any surface defect that can act as a stress concentrator. Mechanical notches are more dangerous than in pure fatigue due to the plastic deformation caused at the notch. Plastic deformation would damage any passive film and accelerates locally the anodic dissolution of the metal [31].

As far as localized corrosion in DSS, Cr, Mo and N will prevent it while Ni will act as an austenite stabilizer. In lieu of this, an equation has been proposed to establish the pitting corrosion resistance in terms of the Pitting Resistance Equivalent Number (PREN) [31]:

$$PREN = \%Cr + 3.3(\%Mo) + 16(\%N) \tag{5}$$

The PREN may be used as a qualitative ranking among different wrought stainless steels. It is necessary, though, to consider the pitting resistance of each phase (ferrite and austenite) individually, specially when heat treatments have been performed since one of the phases may be depleted in Cr, Mo or N as a consequence of aging. Recently, a new microelectrochemical method has been implemented to pursue the pitting corrosion behavior of isolated phases in super DSS's [33]. The studies are in good agreement with PREN calculations on annealed samples with minimum precipitates. The same authors have proposed to study the effect of precipitates within isolated phases on the corrosion resistance of super DSS's and the correlation to their respective PREN number. This may not only increase the understanding of pit (or crack) initiation sites but also crack propagation along the microstructure, i.e., transgranular vs. intergranular cracking. Typically, corrosion fatigue of DSS's have been reported as transgranular [34, 35].

As far as crack initiation goes, Magnin et al. [36] have indicated that a fatigue crack would take place in austenite under low strain amplitude while ferrite will become the initiation site at high strain amplitude. Bassidi et al. [34] have established that austenite grains act as initiation sites due to the extrusions produced by cycling during plastic deformation of low yield strength of this phase. Then, austenite serves as a crack arrester during propagation, i.e., transgranular cracking.

Lattinen and Hanninen [37] pointed out that the stress corrosion cracking (SCC) resistance seemed to be determined by the selective dissolution of one of the phases to corrosion. Newman [38] has indicated that if the potential of a crack tip is below its critical potential for crack initiation but at the optimal crack propagation potential for the second phase, the crack will propagate in the susceptible phase and, consequently, will be arrested by the non-susceptible one. Nonetheless, systems usually sensitive to intergranular cracking during SCC, in fatigue-corrosion are typically transgranular under high cyclic loading or when strains are very rapid. This clearly shows that, depending on the loading conditions, the initiation mechanisms in corrosion fatigue can be either similar or totally different from those of SCC [24].

The present study is aimed at furthering the current understanding of corrosion fatigue behavior of DSS after heat treatment and how second phase particles may affect suction roll performance under a white-water environment. The main objective of the present study is to show the effect of heat treatment and resulting microstructural changes on the corrosion fatigue behavior of a DSS in chloride containing white water in paper mills.

2. EXPERIMENTAL PROCEDURE

Onset of crack propagation and crack growth rates were monitored as a function of stress intensity factor "K". Compact Tension (CT) specimens were machined in accordance with ASTM-399 standard for plain-strain fracture toughness of metallic materials as shown in Figure 4 [22]. The specimens were machined with L-R orientation from centrifugally cast DSS roll material (C-0.06, Si-0.92, Mn-0.76, P-0.030, S-0.006, Cr-19.15, Ni-5.23, Mo-2.01, Cu-3.70 in wt%) produced via centrifugally casting. Three different heat treatments were given to the CT specimens, namely HT1, HT2 and HT3 (Table 1). Heat-treated specimens were tested in the white water environments listed in Table 2. All aqueous tests were conducted at 50 °C.

All fatigue tests were carried out in accordance with ASTM 647 [23] using an MTS machine (see Figure 5). A sample is placed in the cross-head section of the machine and held by two cylindrical pins at the upper and lower portions of the sample. Special precautions are taken to electrically isolate the sample from all other metallic parts. Then, the cross head is lowered into a hot bath with the test solution. The tests were conducted at a frequency of 25 Hz, using a sinusoidal waveform and ratio of minimum to maximum stress, $R = \sigma_{min}/\sigma_{max}$, of 0.5.

The method involves constant-load-amplitude cycling load of notched specimens that have been acceptably precracked in fatigue. Crack length is measured in situ using both a stage-mounted long distance microscope with a resolution of 0.001 mm and a stroboscopic light source. The measurement is carried out as a function of elapsed cycles, and these data are subjected to numerical analysis to establish the rate of crack growth. Crack growth rates are expressed as a function of the stress intensity factor change, ΔK, which is calculated for expressions based on linear elastic stress analysis. After each test, the samples were polished and etched, for further examination using an optical microscope. In order to quantify the relative yield strength of the samples, Vickers micro hardness measurements were carried out close to the crack path, but away from the plastically deformed zone. A significant number of measurements were performed on each sample to yield a statistically representative average of the hardness after each heat treatment. Table 3 shows the test matrix used for the study.

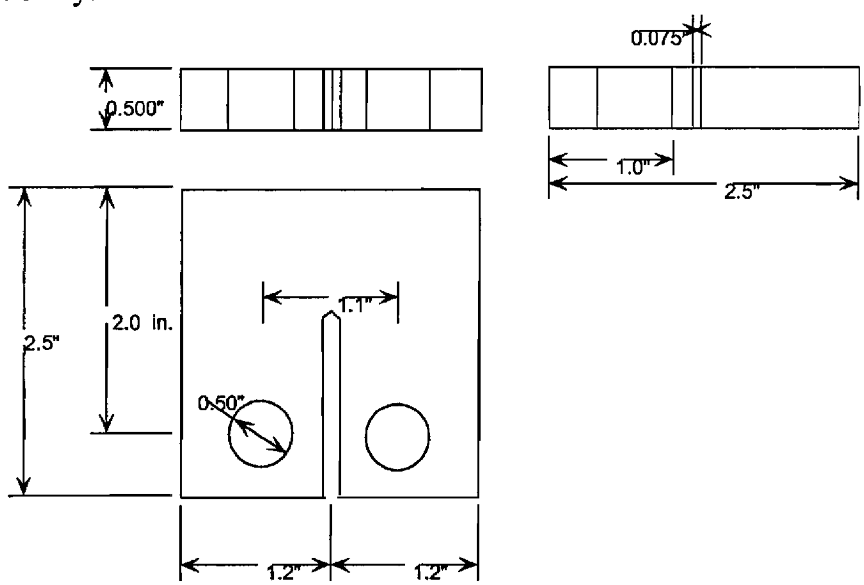


Fig. 4. Compact tension (CT) specimen dimensions used for corrosion fatigue tests.

Table 1. Heat Treatment used for corrosion-fatigue testing of DSS's.

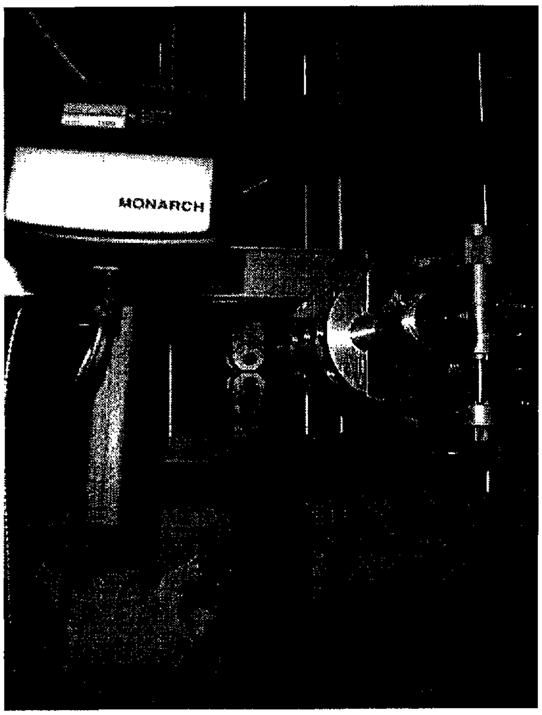
Heat Treatment	Description
*HT1	Aging at 800 °C for 8 h, furnace cooled to room temperature.
*HT2	Solution annealing at 1100 °C for 8 h, water quenched.
*HT3	Solution annealing at 1100 °C for 8 h, water quenched; stress relief annealing at 630 °C x 45 m, air cooled; second stress relief annealing at 560 °C x 45 m, air cooled.

*HT: Heat Treatment

Table 2. Environmental conditions in mg/L.

	SO_4^{-2}	$S_2O_3^{-2}$	Mg^{2+}	Cl^-	Ca^{2+}	Na^+
Air	N/A	N/A	N/A	N/A	N/A	N/A
*WW1	2100	<10	12	200	820	175
*WW2	2100	<10	12	2000	820	1975

*WW: White Water



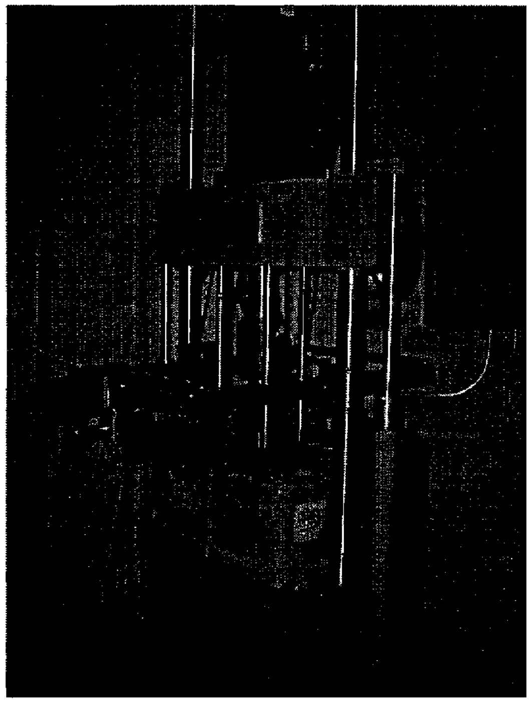


Fig. 5. MTS machine used for corrosion-fatigue tests.

3. RESULTS AND DISCUSSION

Figures 6(a), (b) and (c) show the microstructures of DSS's used in this study after different heat treatments designated as HT1, HT2 and HT3, respectively, as described in Table 1. Figure 6(a) shows that very fine second-phase particles were precipitated mostly along the grain boundaries in ferrite phase after aging at 800°C for four hours followed by slow cooling. Some precipitates were also observed within the ferrite grains. Because of the ability of Villela's reagent to exhibit carbides and sigma phase, it is believed that the precipitates, after HT1 heat treatment, were carbide compounds. However, the reagent did not reveal similar precipitation after HT2 and HT3. Microstructural features after HT2 and HT3 were very similar, as shown in 6(b) and 6(c).

Figure 7 shows the crack growth rate vs. the stress intensity change ahead of the crack tip for all conditions tested. Results summarized in Table 3 and in Figure 7 indicate that the heat treatment plays a significant role in the threshold cyclic stress intensity range, ΔK_{th}, below which the crack does not propagate in a given environment. In general, HT3, exhibited the lowest threshold stress intensity for crack propagation. However, HT2 always showed the largest threshold stress intensity in every environment tested. These results show that the smallest driving force for crack growth corresponds to HT3 followed by HT1 and lastly by HT2 under all tested environments. Results indicate that microstructural changes and/or residual stresses created during sample heat treatment and/or machining have a significant effect on fatigue behavior of DSS's alloys.

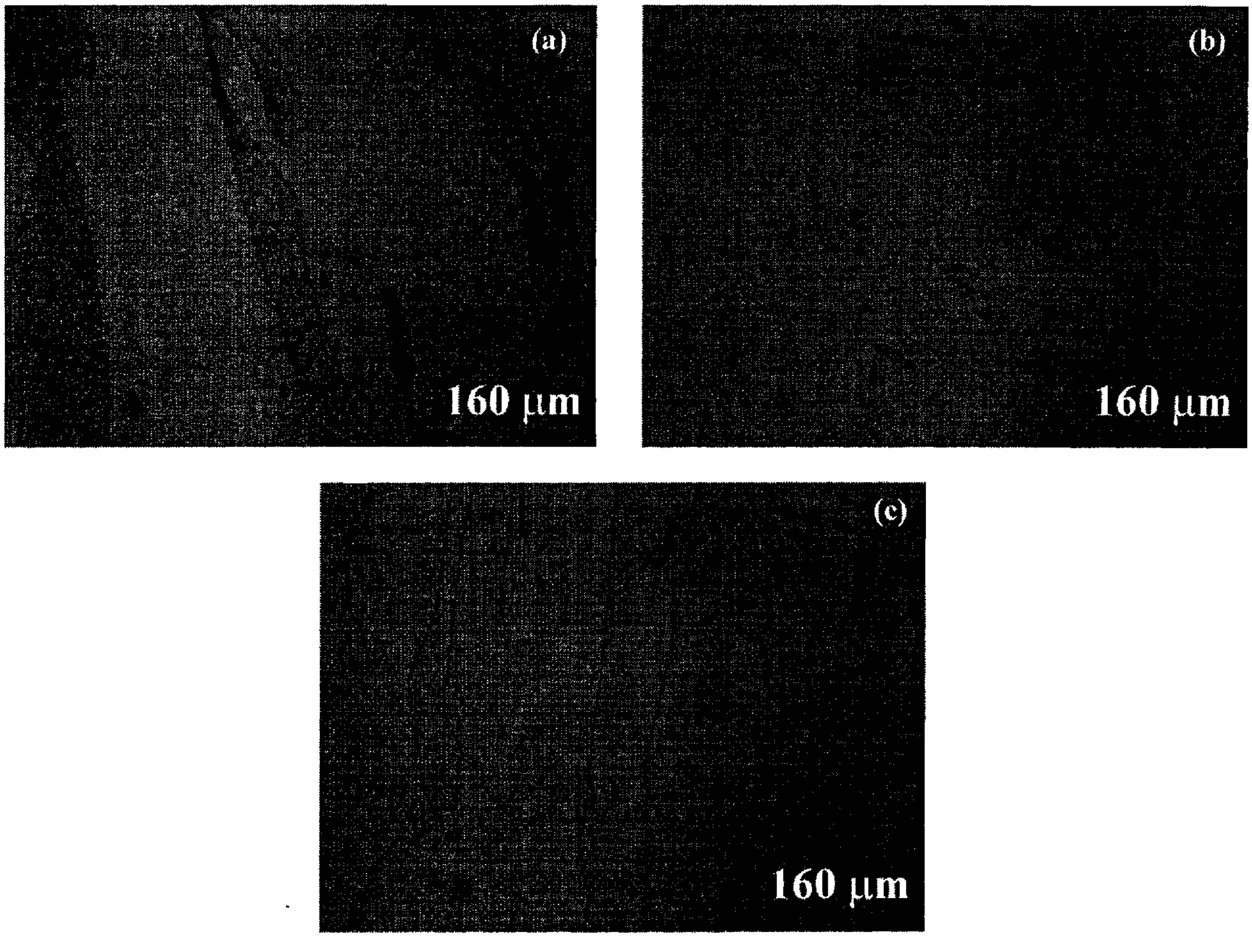


Figure 6. Microstructure of DSS after different heat treatments: (a) after HT1, (b) after HT2 and (c) after HT3

By using Eq. (3) [14, 21] and plotting the results on a log-log scale, the crack growth rate was obtained using a linear least-square fitting procedure. Then the parameters "C" and "m" were obtained from the linear relationship (as well as the best-fit parameter "r^2"):

The parameter "m" indicates the rate at which a crack grows per cycle (da/dN) at a given stress intensity change (ΔK), the driving force for crack growth. The larger the parameter "m", the higher the crack growth for a particular heat treatment in a given environment. In general, HT1 presents the largest "m" values for all three environments tested, followed by HT3 and lastly by HT2. Microstructural features like second-phase particles, only observed with HT1, are expected to strengthen the material since they may act as barriers for dislocation movement produced during localized plasticity of the material. This may also explain the larger threshold stress intensity changes, ΔK_{th}, and larger crack growth rates (with respect to stress intensity change), "m", observed in samples heat treated to HT1 with respect to HT3 (precipitate free and stress relieved).

Figure 7 shows da/dN vs. ΔK for differently heat-treated DSS compact tension samples tested in three different environments. With a few exceptions like HT1 and HT3, samples tested in environment WW1 air seems to have the largest stress intensity threshold, ΔK_{th}, for a given heat treatment (Table 3). Combining results obtained in Figures 7(b) and 7(c) it can be concluded that when the material is exposed to white-water environments, the threshold seems to be lowered with increase in Cl^- content. However, the effect is not significant and is within the error of the measurement.

HT2 and HT3 samples, have a relatively homogeneous structure with no second phase particles observed, with very similar microstructure as shown in Figures 6(b) and 6(c). However, larger thresholds, ΔK_{th}, and smaller crack growth rates, m, were observed for samples heat-treated to HT2 compared to HT3 (and HT1) (Table 3). Differences between HT2 and HT3 heat treatments are found in the stress relief treatment performed on HT3 samples at 650°C for 45 minutes followed by 560°C for 45 minutes. During this treatment and during air cooling, α' precipitates are expected to cause embrittlement in DSS's [24-26, 28, 29]. This may increase the yield strength of the material. Although there are some indications, this increase in strength is not totally clear from the Vickers microhardness measurements due to the larger scatter shown in Table 3. The α' precipitates formed on HT3 heat-treated samples are very small in size and require TEM to resolve them. Metallographic preparation of the failed samples after each test revealed that crack growth seems not to favor any particular phase and is transgranular in mode. However, cracks also show a more tortuous path for HT1 when compared to HT2 and HT3 samples.

Table 3. Summary of corrosion fatigue experiment results.

Condition	**HT**	**Environment**	**pH**	**ΔK_{th}**	**m**	**r^2**	**HV±STD**
CT1	HT1	Air	N/A	17.7	3.85	0.94	283±30
CT4	HT2	Air	N/A	23.2	1.57	0.72	247±23
CT7	HT3	Air	N/A	12.2	2.38	0.85	258±24
CT2	HT1	WW1	6.8	15.8	1.72	0.97	283±30
CT5	HT2	WW1	7.1	27.9	1.59	0.96	247±23
CT8	HT3	WW1	6.7	12.7	1.67	0.77	258±24
CT3	HT1	WW2	6.9	14.1	3.29	0.77	283±30
CT6	HT2	WW2	6.9	20.0	1.60	0.64	247±23
CT9	HT3	WW2	6.7	11.3	2.59	0.77	258±24

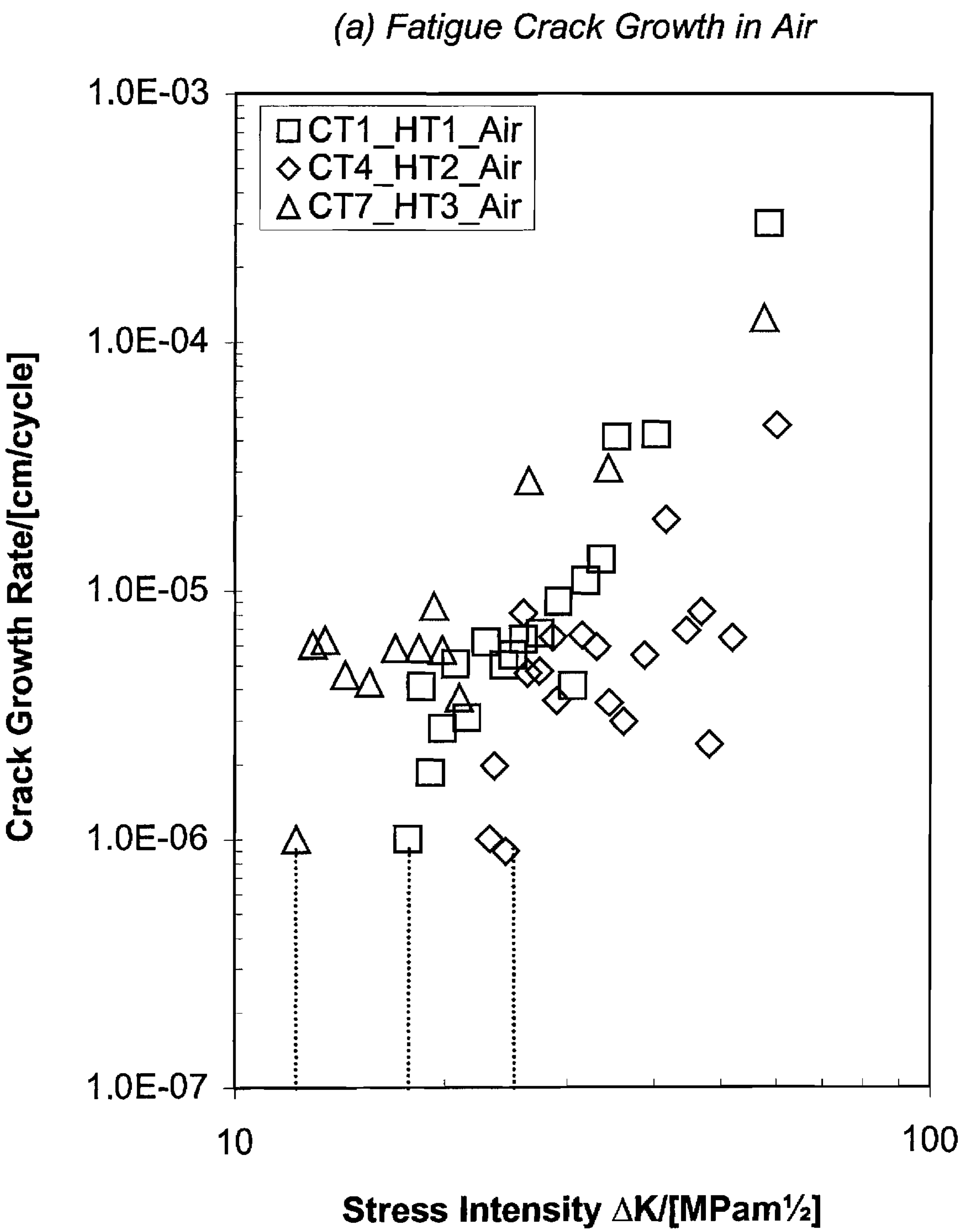


Fig. 7(a). Fatigue crack growth in air

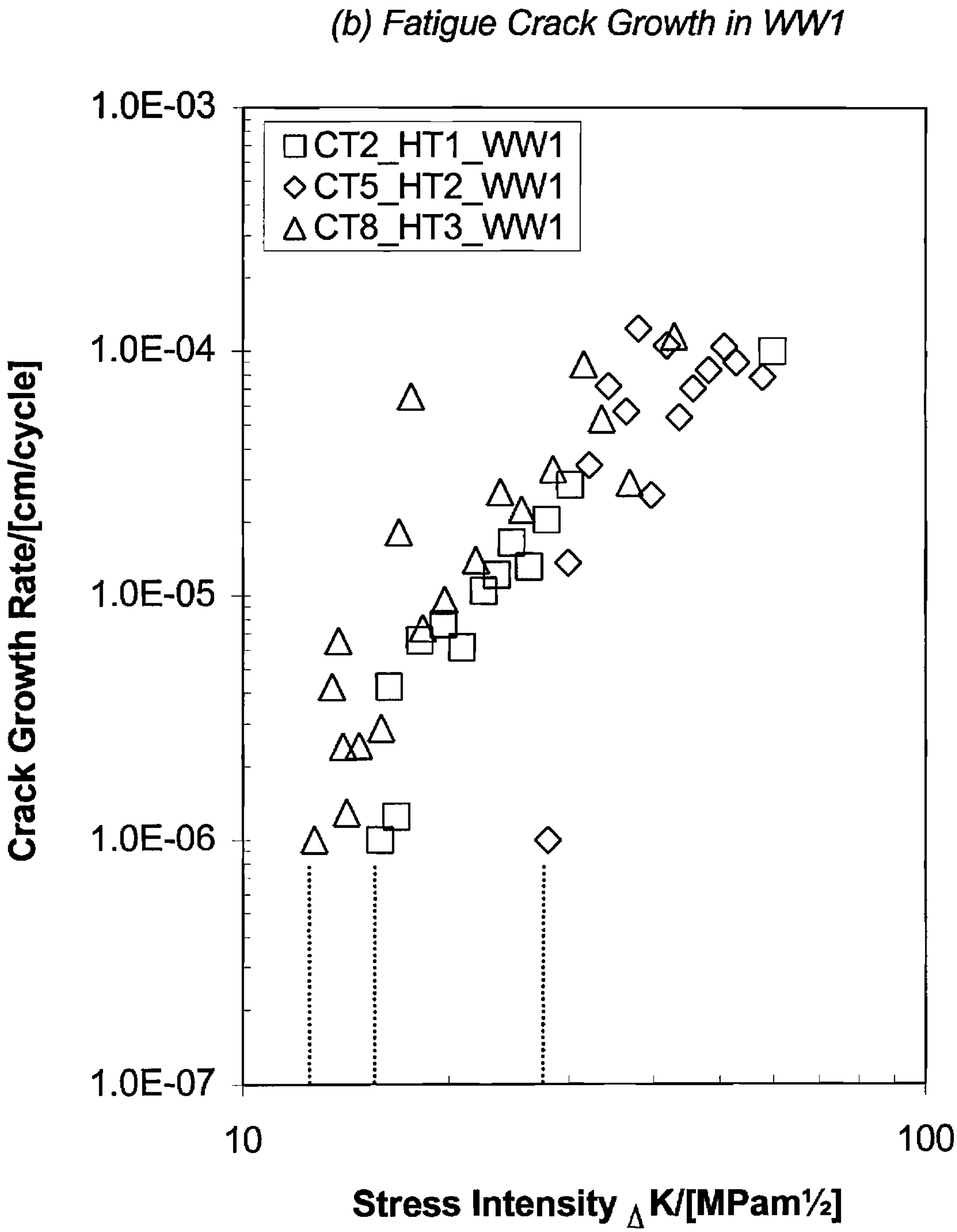


Fig. 7(b). Fatigue crack growth in WW1.

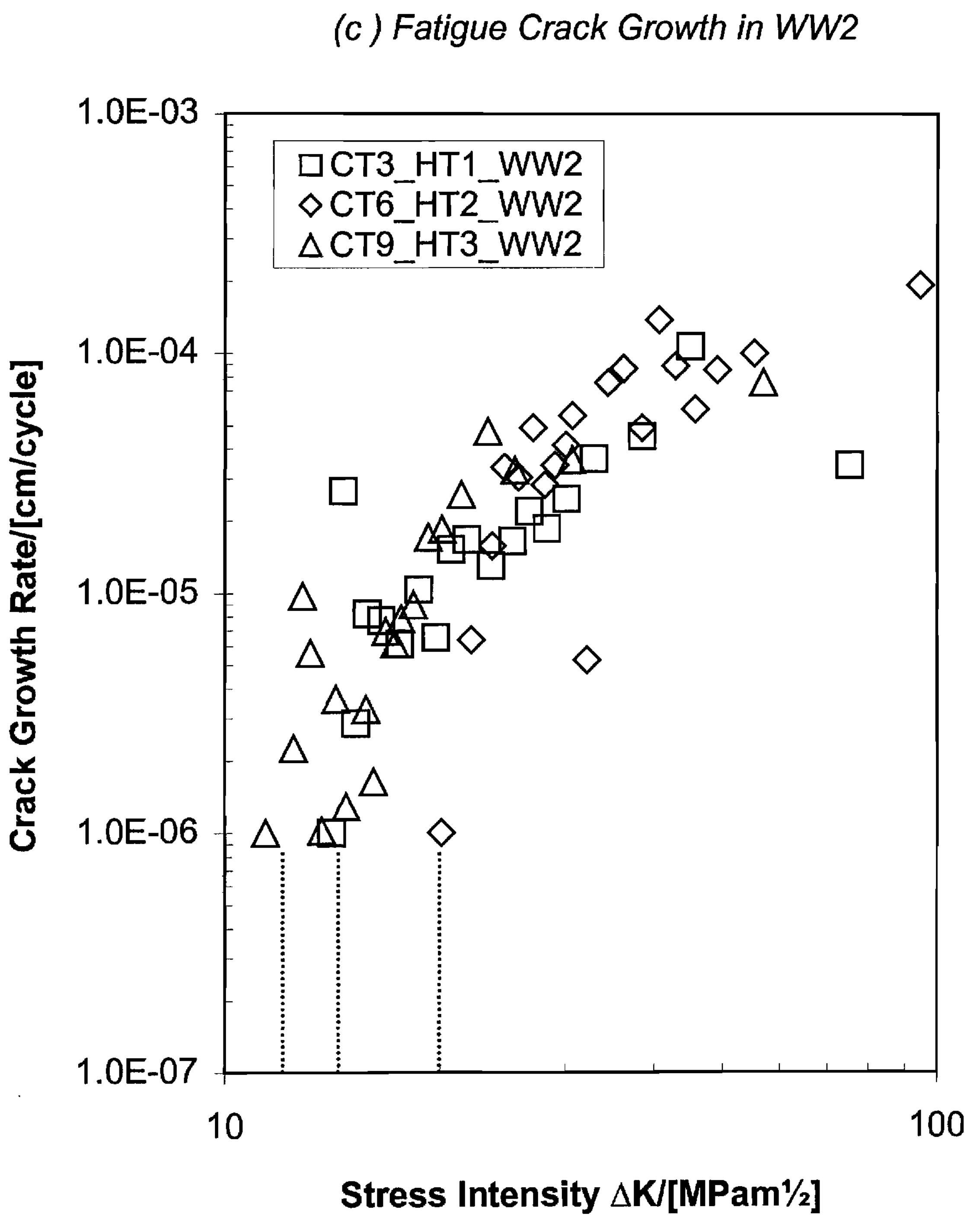


Fig. 7(c). Fatigue crack growth in WW2.

4. CONCLUSIONS

Microstructural changes arising from heat treatment conditions produced during manufacturing or during operating conditions of DSS suction roll materials may affect their fatigue behavior. Results from this study clearly indicate that for the tested duplex stainless steel, microstructural changes due to heat treatment had more effect on the threshold stress intensity for crack propagation and on crack growth rates than did an increase in chloride ion concentration in paper mill environments.

Increase in chloride ion concentration had a small effect on lowering of threshold stress intensity change, ΔK_{th}, for all heat treatments; however, one of the reasons for the insignificant effect of the environment on corrosion fatigue behavior of DSS's might be the test parameters. The experiments presented in this study were conducted at 25 Hz in a tension/tension sinusoidal waveform of R=0.5 ($R = \sigma_{min}/\sigma_{max}$). Under high frequency the crack tip may not be exposed to the aggressive environment for long enough time to be affected in terms of propagation and growth rates. Lower cycling frequencies will expose the crack opening for longer periods to the aggressive environment and may exhibit a detrimental effect on the corrosion-fatigue crack behavior.

Environments, which cause localized corrosion in DSS (e.g., higher chloride ion concentration in white waters), may show a significant effect on the fatigue life of DSS rolls as pits may act as initiation sites for cracks as well as precipitates in crack growth. This effect may also be more pronounced at lower frequencies as the crack tip will be exposed to the corrosive environment for longer time periods in each cycle.

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